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# MICRONIC CAPACITOR

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*COURTER ELECTRIC PRODUCTS, INC.*

*FEBRUARY 1954*

WRIGHT AIR DEVELOPMENT CENTER

# MICRONIC CAPACITOR

*Ralph F. Hoeckelman*

*Courter Electric Products, Inc.*

*February 1954*

FOREWORD

This report was prepared by Ralph F. Hoeckelman of the Courter Electric Products, Inc., Boyne City, Michigan, on Air Force Contract AF 33(600)-22909 under Project No. 4155, "Micronic Capacitors for Transistors," and summarizes the research for the period of February 15, 1953 to February 15, 1954. The work was administered under the direction of the Electronic Components Laboratory, Directorate of Research, Wright Air Development Center, with Mr. Albert C. Speaks acting as the project engineer. He was later succeeded by Mr. Roger L. Faust.

Investigations of techniques and materials are being continued and will be reported from time to time.

## ABSTRACT

Preliminary investigations leading to a small, lightweight micronic capacitor which would perform at high temperature are outlined. Special laboratory equipment and techniques are described, and experimental tests and evaluations of various dielectric materials are presented.

## PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:

RICHARD S. CARTER
Colonel, USAF
Chief, Electronic Components
Laboratory
Directorate of Research

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# I. INTRODUCTION

The idea of a micronic capacitor composed of evaporated thin films of metals and dielectric materials originated late in 1950. Early in 1951, Mr. Reefman contacted the Weapons and Components Division of the Wright Air Development Center in regard to this disclosure. No capacitor then available had a high temperature potential equal to that of a quartz dielectric capacitor.

Somewhat later that year, Courter Electric Products, Inc. began work on the development of the micronic capacitor. After many fruitless attempts to build capacitors with evaporated quartz, sapphire, zircon, titanium oxide, or magnesium fluoride dielectrics, several successful capacitors were produced using silicon monoxide as a dielectric material. The "bugs" were never successfully overcome and the capacity of single sandwich units was disappointingly low. The excessive handling and time consuming steps performed in the fabrication of these units made them uneconomical.

The original idea appeared to be sound as good quality capacitors were actually produced. The realization that a considerably longer program involving the expenditure of a sizable research and development fund prompted the closing of this work.

The status of the work was brought to the attention of the Weapons and Components Division of the Wright Air Development Center. This contract is a result of the conferences held to discuss the research and development of a micronic capacitor. The program as outlined in the exhibit provides for a four phase program covering a period of three years. This summary report covers a substantial part of the initial phase of the program.

# II. EXPERIMENTAL PROGRAM

The experimental work was divided into several areas of investigation. The first area of investigation was the evaluation of dielectric materials by surveying the literature and by experimental tests. The investigation was limited to inorganic dielectrics.

The second area of investigation was the study of techniques and the determination of properties of the various capacitors produced. The techniques for controlling the thickness of films, quality of films, and post evaporation requirements to produce uniform good quality capacitors were studied. The evaluations of dielectric constants, dielectric strength, temperature coefficients, and aging characteristics were made.

The third area of investigation was essentially physical. The problem of obtaining a large capacity in a small space was studied. Handling, holding, masking, and packaging were investigated.

# III. APPARATUS

All experimental work on this contract was conducted in a special laboratory 29 ft by 12 ft. The laboratory was air conditioned to eliminate dust and oil particles from the working area. The room was kept at constant temperature by a Bard oil burning furnace and an Armstrong cooling unit. All air whether intake or recirculated was passed through a Trion electrostatic air cleaner. The dust content of the air in the laboratory was considerably below that encountered in the rest of the plant.

All of the experimental filming tests were performed in a Distillation Products, Inc. (Consolidated Vacuum Corp.) vacuum coater, model LCI-14. The vacuum coater contains two Welch Mechanical Pumps Type No. 1403 which serve as roughing pump and holding pump. The diffusion pump is a DPI model MC-275 capable of producing a vacuum of $5 \times 10^{-5}$ mm Hg pressure. The diffusion pump is connected to the evaporation chamber by a straight section of steel pipe containing a DPI model VTSB-4 high vacuum valve. The pressure is measured by a Pirani and a Phillips gauge. The vacuum coating chamber is 14 inches in diameter and 24 inches high. The steel base plate contains 9 insulated feed-throughs for conducting electrical power to the inside of the unit. A 2 KVA Variac voltage control and fixed step-down transformer supply the power for evaporation. An auxiliary 2 KVA Variac voltage control and fixed transformer supply power for additional operations such as simultaneous evaporation, heaters, etc. A Stokes No. 276 AC Vacuum gauge is used to calibrate the Pirani and Phillips gauges and to measure pressures in a small additional vacuum chamber.

Visual examination of evaporated films may be made at magnifications of 60 to 460 times as seen through the Bausch and Lomb metallurgical microscope. Photographic attachments are available for recording the appearance of the films.

A Christian Becker analytical balance measures weight gains and losses of filaments, crucible contents, glass substrates, etc. The balance is a valuable tool to assist in measuring film thickness, angle of evaporation, i.e., dispersion, efficiency of operation, and amount of adsorbed contamination.

Capacitors are tested electrically for capacitance, resistance, and dissipation factor. The initial resistance measurement is made with a Simpson test set. Additional resistance measurements are made at voltages of 100 vdc to 600 vdc by an Industrial Instruments megohm tester. The capacitance and dissipation factor are measured on a General Radio Company Impedance Bridge balanced with the aid of a Heathkit vacuum tube voltmeter.

The post evaporation heat treatments of capacitors are performed in an Electrikiln oven regulated by a Bristol temperature controller.

Facilities available in the special laboratory include 110 vac power, hot and cold water, and compressed air. The services of a small model machine shop are available including hardware and tools.

# IV. PROCEDURE

## Preparation of Substrate

Glass substrates were used in most of the experimental work. Several different types of glass in different sizes and thicknesses were evaluated. Small steatite ceramic plates, brass, and tantalum were also used for substrates in several tests to determine the most promising base material. Glass appears to be the best all-around substrate because of its lightness, smoothness, hardness, availability at low cost, and satisfactory performance.

Pyrex or plate glass substrates 1/16 in. to 3/16 in. thick were scrubbed with Alconox detergent, washed with hot water, rinsed in acetone, and dried. The glasses were visibly clean. Microscopic examination revealed some imperfections mainly in the glass surface itself. The seeds, striae, etc.,present in the surface of the glass were more pronounced defects than dirt or dust particles remaining on the glass. The gross imperfections in this glass led to a desire for much smoother glass substrates. Other tests indicated the limited capacity of silicon monoxide base capacitors and the desirability of stacking several units in parallel. Thus, thin glass substrates would also be beneficial. To achieve both the desired smoothness and thinness, optical cover glasses were chosen for the substrate material. These glasses are available in large quantity at reasonable price and are quite thin and free from seeds and other surface imperfections.

The thin fragile nature of the optical cover glass forced the abandonment of the original cleaning process. A new chemical cleaning process was used to replace the scrubbing technique. The glasses were dipped in hot chromic-sulfuric acid, washed in hot water, rinsed in acetone, and dried. The glass surface appeared clean and free from dust and stain when viewed under the high magnification of the microscope. This cleaning process is the standard technique adopted for cleaning optical cover glass substrates.

## Operation of the Vacuum Coater

The bell jar was raised two feet above the base plate and locked in position. Filaments and material to be evaporated were placed in position. A rack holding the substrates was placed over the filaments. Shields, heaters, or other devices were put in place and the bell jar was lowered over the entire assembly. The air vent to the vacuum chamber was closed, the valve to the roughing pump opened, and the roughing pump turned on. The holding pump and diffusion pump were turned on or may have been left on from the previous run,since the vacuum valve isolates the diffusion pump from the bell jar.

The Pirani and Phillips pressure gauges were turned on. When the pressure in the bell jar became lower than 50 microns pressure, the valve to the roughing pump was closed and the valve to the diffusion pump was opened. When the pressure reached 0.3 microns the

filaments were outgassed and heaters, if any, were turned on. The shields were removed and when the pressure reached 0.1 to 0.2 microns Hg, evaporation was begun. At the end of the evaporation period all power to the bell jar was turned off, the valve to the diffusion pump closed, and the air vent opened. The rack with the filmed substrates was removed. The pump down period exclusive of the filming operation requires one to one and a half hours.

## Evaporation of Metals

Aluminum, copper, nickel, chromium, and nichrome were evaporated by several different methods. Aluminum is the easiest metal to evaporate because it boils at a low temperature, wets a tungsten filament, and its soft ductile nature makes it easy to attach to the filament. Aluminum alloys with tungsten and limits the amount of metal that can be evaporated from a given mass of tungsten. The rate of evaporation is also important, since any metal which evaporates is no longer available for alloying. The aluminum evaporates from the alloy and redeposits tungsten on the filament but not exactly in the same place from which the tungsten was originally removed. The filament acquires an irregular cross section and limits the life of tungsten filaments.

Copper did not wet tungsten or molybdenum filaments but melted and dropped from the filaments before any substantial quantity could be evaporated. A tungsten filament embedded in copper powder fused the powder together and shorted out the filament. Copper could not be evaporated in this way. A very fine copper wire wrapped around a tungsten filament gave much better results because appreciable evaporation took place before the molten copper agglomerated in drops of sufficient weight to break loose from the filament. Best results were obtained by electroplating copper directly onto the filament. Rapid evaporation from copper coated filaments produced satisfactory copper films.

Nickel alloyed with tungsten resulted in burned out filaments. Nickel could be evaporated by placing nickel powder in a crucible, heating the tungsten filament to a dull red, and touching the powder momentarily. The filament containing a small amount of nickel was heated white hot and the nickel boiled off. The process was repeated until the desired thickness was obtained.

Chromium powder placed in a crucible was evaporated by slowly raising the crucible so that the powder just touched a white hot tungsten filament. Evaporation was slow because the fused chromium powder conducted the heat away rapidly and shorted out the filament. Chromium was evaporated easily from a tungsten filament covered with an electrodeposited chromium film.

Nichrome, a chromium-nickel alloy, was evaporated easily from tungsten filaments. Nichrome wet the tungsten filaments and alloyed to some extent but substantial amounts of nichrome could be evaporated without burning out the filaments.

## Evaporation of Dielectrics

All of the dielectric materials were available in powdered form. Tungsten filaments were embedded in these materials and heated to the evaporation or decomposition temperature. These materials were generally composed of light weight and sometimes finely divided particles. A very rapid evaporation almost certainly carried massive particles in the vapor stream which hit and damaged the films on the substrate. The dielectrics were evaporated at a much slower rate than the metals.

Unstable oxides attacked the tungsten filaments at high temperatures causing burn outs. This problem was not serious, since unstable oxides produced very poor dielectric films. Oxides generally evaporated or decomposed without melting. Fluorides generally melted before evaporation. The dielectrics which melted shrank in volume and pulled away from the filament. The crucible containing a molten dielectric was raised so that the filament again touched the dielectric.

When a combination of dielectrics was desired, the mixed dielectric was placed in one crucible and the mixture heated. Another method of producing a combination dielectric film was the simultaneous evaporation of dielectrics from different crucibles. A third method of producing a composite dielectric was the filming of alternate layers of different dielectrics.

## Post Evaporation Technique

Films were treated to improve the electrical characteristics, hardness and abrasion resistance. Heat treatment was the most effective method of improving the quality of films. Capacitors were placed in a steel rack and the rack was placed in a thermostatically controlled oven. The heat treating periods varied from 15 minutes to 15 hours. Heating in vacuum and in steam atmospheres were variations of the heat treating process. Capacitors were placed on a ring heater in a small vacuum chamber. The heater was controlled manually by voltage control equipment, and a thermocouple and potentiometer measured the temperature attained. A steam atmosphere was obtained by placing the capacitor in a chamber containing boiling water. Chemical treatments of the surface, such as water washes or immersion in oxidizing agents, were generally ineffective. Lengthy aging periods affected the properties of the films.

Another type of post evaporation treatment was the electrical conditioning or aging. When a voltage was applied to the capacitor, the properties changed for a period of time after which the change became progressively slower. The change in properties was essentially similar to that produced in the heat treating and aging processes. These methods supplemented each other. No one single method of treatment produced the change of properties that a combination of treatments produced.

## Testing Procedure

Capacitors were tested with the Simpson test set. Good quality capacitors measured infinite resistance. Occasionally capacitors were shorted out or had low resistance. Any capacitor having low resistance, i.e. below 1 megohm, on the Simpson test set could not be tested satisfactorily on the bridge because the unit acted as much like a resistor as a capacitor. Capacitance readings in such cases meant nothing.

After the capacitors had been tested on the Simpson test set, they were placed in the bridge circuit and the capacity and dissipation factors measured. The bridge was balanced with the aid of a vacuum tube voltmeter. The capacitor was next placed on the megohm tester. A voltage of 100 vdc was applied to the unit. For the first few minutes during the initial period of testing, the resistance climbed but gradually stabilized at a peak value. The capacitor would reach the peak value quite quickly after the initial aging period. If the leads were reversed, a longer time was required to reach peak resistance than if the capacitor were always charged in the same direction. The resistance readings were not always identical in both directions. The original position generally gave the highest peak resistance possibly indicating some type of polarization.

The same instruments were used in making measurements under vacuum or at high temperature or other condition.

The thickness was tested by a weight determination before and after filming. The weighings were made on a standard analytical balance. The capacitors were clean and dry when weighed.

A visual inspection of the capacitors revealed the over-all quality. Peeling, improper masking resulting in misplaced films, and mirror quality were easy to detect with the naked eye. A microscopic examination revealed minute cracks, dust particles, agglomerates, or other defects.

## V. RESULTS

### Metal Films

Vacuum coating of objects has been a commercial enterprise for quite a few years. Mirrors, reflectors, toys, and door knobs have all been metallized by thermal evaporation in vacuum.[1,2] Moderately high boiling metals produced the best films and, fortunately, these metals possess good electrical conductivity and sufficient hardness.[3] Aluminum, chromium, copper, gold and silver were evaporated.[4]

Aluminum, copper, nickel, chromium, and nichrome were thermally evaporated in the vacuum coater. All of these metals produced smooth adherent coatings on a glass surface. Each metallic film was characterized by its own properties. Aluminum was soft, highly conducting, and could be deposited in thick layers. Chromium was hard, fairly

conductive, and could be deposited in an adherent film up to 1000 $\overset{o}{A}$ thick. Aluminum, copper, and nickel had high coefficients of thermal expansion,while chromium had a low coefficient of expansion. The initial metal film had to adhere tenaciously to the glass base and possess hardness and durability as we.. as a low coefficient of thermal expansion. Chromium was ideally suited as a base for the dielectric film except for the brittleness which limited the thickness of adherent chromium films. The metal film serving as a dielectric base was composed of nichrome followed by pure chromium. This combination of metals allowed substantial film thicknesses to be applied without peeling or blister formation.

The final metal film covering the dielectric had to be soft and ductile to aid in "burning out" or self healing of weak spots in the capacitor. The final metal film had to adhere to the dielectric and had to be able to withstand the 400°F heat treatment imposed upon the finished unit. An aluminum film gave good results.

### Dielectric Films

The first major area of investigation was the evaluation of dielectric materials. The oxides which make good dielectrics are very high melting, high boiling materials. The evaporation of these oxides is a difficult problem because their boiling points approach the boiling point of the heater elements. The heaters are subject to burning out due to melting, evaporating, or chemical reaction with the oxides. Many of the oxides are unstable in vacuum at such high temperatures. Moreover, most of the oxides do not possess good wetting characteristics. However, such oxides as silicon monoxide and fluorides such as magnesium fluoride have been evaporated successfully.[5,6]

Two classes of dielectrics were investigated, the salts and the oxides. The salt type dielectrics will be discussed first. Salts generally have very high dielectric constants as compared to the common organic type dielectric used in many commercial capacitors. The dielectric constants of various salts are listed below.[7]

| Salt | Dielectric Constant | Salt | Dielectric Constant |
|------|---------------------|------|---------------------|
| Li F | 9.3 | Rb Cl | 5.0 |
| Na F | 6.0 | Rb Br | 5.0 |
| Na Cl | 5.6 | Rb I | 5.0 |
| Na Br | 6.0 | Cs Cl | 7.2 |
| Na I | 6.6 | Cs Br | 6.5 |
| K Cl | 4.7 | Th Cl | 32 |
| K Br | 4.8 | Cu Cl | 10 |
| K I | 4.9 | Cu Br | 8 |

The dielectric constants of the salts listed are generally 5.0 or above in contrast to the dielectric constants of most of the organic materials which are below 5.0. The advantage of using a material with a high dielectric constant is obvious. A salt dielectric with a dielectric constant 2 to 5 times greater than that available in a competitive capacitor would hold 2 to 5 times as much charge for a given thickness of dielectric. The thermal evaporation process might give more uniform films than those obtainable by rolling or other processing and thus may be made 1/2 to 1/10 as thick as conventional dielectrics. A salt dielectric capacitor may have 10 to 50 times the capacity of a comparable commercial capacitor.

Of course, many other properties are as important as the dielectric constant. The electrical resistance of solid state salts is high if they are not made conductive by solution in water. The extreme hygroscopic nature of many salts limits their usefulness. However, some salts are not hygroscopic. The fluorides are essentially non hygroscopic and magnesium fluoride is being used commercially in the coating of lenses.

Still other important factors are chemical stability and dielectric strength. The salt must be stable so that it does not undergo decomposition during the filming operation. It must also be stable in contact with the metal films of the capacitor. The salts should be composed of halides of active metals so that the metallic part of the salt will be less noble than the metal used as capacitor plates.

Of the vast number of possible salts available, magnesium fluoride and lithium fluoride were selected for the first choices because of their chemical stability, non hygroscopic nature, and high dielectric constant.

Magnesium, calcium, barium, and strontium fluorides have been evaporated.[8] Although fluorides have been evaporated by many people, the properties of the films are not completely known with respect to evaporation technique, type of substrate, post evaporation treatments, etc. Cameron[8] states "Barium fluoride appeared to adhere better than calcium fluoride, although it was no improvement from the chemical standpoint, since all the coatings were porous." Schulz[9] has shown that evaporated salt films are composed of crystals with considerable voids throughout the film. Salt films with appreciable voids would not be expected to provide good insulation resistance or dielectric strength. However, this assumption had to be verified by experimental evidence.

Magnesium fluoride and lithium fluoride were obtained as powders and evaporated from porcelain crucibles heated by an immersed tungsten filament. Tests of fluoride dielectric capacitors are listed in Table 1.

## TABLE I

### FLUORIDE DIELECTRIC CAPACITORS

| Test No. | Resistance megohms | Capacity m f | D Q | Dielectric | Remarks |
|---|---|---|---|---|---|
| 50A | 0.0 | - | - | $MgF_2$ | Thin crystalline deposit |
| 50B | 0.0 | - | - | $MgF_2$ | Thin crystalline deposit |
| 31 | 0.50 | 0.0674 | 0.235 | 4 layers SiO, 3 layers $MgF_2$ | Alternate layer coating |
| 32 | 4.0 | 0.020 | 0.095 | 3 layers SiO, 2 layers $MgF_2$ | Alternate layer coating |
| 33 | 5.0 | 0.010 | - | 5 layers SiO, 4 layers $MgF_2$ | Alternate layer coating |
| 51A | 10 | 0.0048 | 0.28 | $SiO$-$SiO_2$, $MgF_2$ | Alternate single layers |
| 51B | 10 | 0.00365 | 0.21 | $SiO$-$SiO_2$, $MgF_2$ | Alternate single layers |
| 55 | 0.1 | 0.28 | 1.05 | LiF | Thin coating |
| 57 | 0.4 | 0.33 | 0.9 | LiF | Thin coating |
| 59 | - | - | - | LiF | Thick coating; peeled |
| 61 | 10 | 0.008 | 0.22 | 2 layers LiF, 1 layer SiO | 2 megohms at 90 vdc |

Magnesium fluoride appears to form a crystalline deposit. The dielectric film in test number 50A was deposited on a heated substrate whereas the film deposited in test number 50B was deposited on a cool substrate. In both cases the resistance of the film was less than 100 ohms. By combining the high dielectric constant of magnesium fluoride with the insulation resistance of silicon monoxide a high capacity unit with good insulation might be realized. In tests 31, 32, 33, 51A, and 51B alternate layers of magnesium fluoride and silicon monoxide were filmed in the hope of realizing both high capacity and good resistance. However, as the resistance improved, the capacity dropped so as to offer no advantage over the straight silicon monoxide capacitors.

The lithium fluoride capacitors had properties similar to the magnesium fluoride units. The capacity values were quite high and the resistances were somewhat better than magnesium fluoride units. The combination silicon monoxide-lithium fluoride film in test number 61 had about twice the capacity of a comparable silicon monoxide-magnesium fluoride film of equal resistance. Even this combination offers little advantage over straight silicon monoxide capacitors.

The second type of dielectric material studied was the oxides. The vapor pressures of the oxides are not very well known and many of the reported results are confusing and contradicting. Some oxides boil at quite low temperatures such as arsenic oxide which boils at 730°C. Data from the International Critical Tables state that cupric oxide at 950°C has a vapor pressure of $6.8 \times 10^{-4}$ mm Hg and silver oxide at 1316°C has a vapor pressure of 0.46 mm Hg. The boiling point of silicon dioxide is listed as 2230°C and the boiling point of aluminum oxide is listed as 2210°C. The values of vapor pressures from the International Critical Tables covers wide range of temperatures and pressures. Yet many investigators have claimed that all of the materials listed, i.e., $CuO$, $Ag_2O$, $SiO_2$, and $Al_2O_3$, are unstable at the temperatures listed and the compounds decompose. Brewer and Margrave[10] list three types of oxides distinguished: "(1) by vaporization as a gaseous oxide molecule whose composition corresponds very nearly to that of a solid; (2) by vaporization with partial decomposition to a gaseous oxide molecule of composition differing from that of the solid oxide and metal, or (3) by vaporization with complete decomposition to the elements, i.e., the metal and O or $O_2$ as is appropriate to the temperature. As examples of the first type of vaporization one may use $MoO_3$, SrO, $WO_3$, SnO, and PbO, the second type of reaction is illustrated by $Al_2O_3$ and $SiO_2$, and the third reaction type is that shown by FeO, MnO, ZnO, CdO, and NiO."

Many of the difficulties of determining the vapor pressure of an oxide at some given temperature can be appreciated by realizing the many possible environments and methods of measurement used. An oxide stable in air at a given temperature might decompose if placed under high vacuum. An oxide might react chemically with the walls or container or measuring device. And again decomposed oxides might recombine in cooler portions of the apparatus creating false impressions of evaporation.

The problems of predicting vapor pressure or decomposition are not the only problems involved. The suboxides such as silicon

monoxide and germanium monoxide may undergo other reactions. Jolly[11] states that "solid state GeO appears to be unstable with respect to disproportionation. In this respect GeO resembles both SiO and SnO." And Hass[12] says, "If a vacuum-deposited film of silicon monoxide is heated for several hours at $600^{\circ}C$ or more in an inert atmosphere, it decomposes to silicon and silica."

Other problems involved in filming oxides are the ever present problems of purity, evaporation technique or conditions, and post evaporation techniques to alter the properties of the films produced.

Many oxides were evaporated in an attempt to discover the electrical properties of the films. Several classes of oxides and suboxides were studied including the three types of oxides listed by Margrave and Brewer. The first type of oxide listed should be stable and vaporize without decomposition. PbO was listed in this group. In test number 39, a capacitor was prepared of aluminum plates and a PbO dielectric. The yellowish PbO powder evolved a large quantity of gas during the filming operation indicating decomposition. The dielectric film had a grayish metallic appearance. The capacitor had a resistance of 3 ohms. Clearly PbO did not vaporize without decomposition. None of the other oxides listed in group one was studied, since they are not generally recognized as good insulating materials.

The second type of oxide represented by $SiO_2$ should undergo partial decomposition during evaporation. In test number 36, pieces of quartz rod were wedged in between turns of the tungsten filament. The quartz rod became discolored at the hottest sections but essentially no evaporation took place. In test number 37, small particles of quartz were placed in a crucible and a tungsten filament was partially embedded in the quartz. Some of the particles melted and formed a glass cover over the filament wire. Some evaporation took place. The coating was a light amber color. Since the suboxide SiO is brown, it is reasonable to assume that quartz partially decomposed to SiO and oxygen. The film of SiO was partially reoxidized giving a composite coating of SiO and $SiO_2$ having a yellowish color.

In test number 38, a capacitor was built of aluminum plates and a dielectric of evaporated quartz. The dielectric coating had a yellowish brown color. The films produced in this test and in test number 37 were not stable. The dielectric film was not adherent to the glass or to the aluminum film.

Test number 53 was the preparation of a capacitor with aluminum plates and a dielectric of evaporated zircon. Zircon ($ZrSiO_4$) was expected to give results similar to pure quartz. The dielectric film was 6 wave lengths thick and peeled just as other films of evaporated quartz peeled. The electrical tests could not be conducted with any meaning due to the immediate depreciation of the dielectric film.

The third type of oxide which decomposes to metal and oxygen during evaporation is represented by CdO. In test number 40, CdO was evaporated to form the dielectric of a capacitor. The metal plates were aluminum. The brownish red CdO evolved a lot of gas upon heating and the dielectric film appeared gray. The capacitor had an electrical

resistance of 6 ohms. The CdO had decomposed to metal and oxygen before evaporation.

In test number 42, copper oxide, whose vapor pressure was reported to be about 0.7 microns Hg at 950°C, was evaporated as the dielectric layer of a capacitor. A lot of oxygen was evolved at 950°C. Cupric oxide decomposed so easily upon heating that this procedure was later adopted as a standard means of adding oxygen to the vacuum system.

In test number 41, cobalt oxide was evaporated as the dielectric film of a capacitor. The oxide decomposed liberating a large volume of oxygen. A thin transparent film was formed. The resistance of the capacitor was 42 ohms.

In test number 67, antimony oxide was evaporated as the dielectric material between aluminum films. The oxide seemed to boil easily without much outgassing but the dielectric film was black. Some decomposition may have taken place. However the capacity of this unit was 0.0168 mf with a dissipation factor of 0.25 and an electrical resistance of 1 megohm. The dielectric strength was very poor, since the unit broke down completely at 90 vdc.

The results of tests of the various oxides indicated that the oxides as a general rule tended to decompose at high temperature under vacuum before they evaporated. Moreover, films produced from such oxides had low electrical resistance. Oxide impurities of the type which decomposed to metal and oxygen were avoided as much as possible by evaporating only high grade chemically pure dielectrics whenever possible. The inclusion of even small amounts of PbO, CdO, $Co_2O_3$, or CuO in a high grade dielectric would certainly cause the capacitor to have a much lower electrical resistance than it would normally have.

The suboxides are oxides of metals with lower oxygen content than normally encountered with that particular metal. The suboxides in a sense are the resulting products of partial decomposition of the normal oxides. As an example, silicon almost always has a valence of 4 and so the normal oxide is silicon dioxide. The partial decomposition of silicon dioxide causes oxygen to be evolved and a new lower or suboxide to be formed. Silicon monoxide is the usual product of partial decomposition of silicon dioxide. Therefore silicon monoxide can be referred to as a suboxide. Other suboxides of interest are $Al_2O$, TiO, and ZrO. The only suboxide investigated to date is silicon monoxide. The silicon monoxide base capacitors generally have high electrical resistance, fairly high capacity, and reasonable stability.

In tests 24, 26, 28, 29, and 30 silicon monoxide was filmed as the dielectric material between aluminum or copper films. The dielectric films were quite thin and the capacity was 0.03 m f per square inch. The electrical resistance was about 1 megohm for a 0.03 m f capacitor. The silicon monoxide film appeared to be stable and offered fairly high capacity values. The electrical resistance was low but appreciably better than most of the other materials tested. The electrical properties were altered readily by heat treatment, evaporation technique, etc. Other dielectric materials might also respond to various techniques but silicon monoxide was selected as

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having the greatest chance of success. Therefore, various techniques were explored in relation to silicon monoxide base capacitors in the hope of producing a capacitor having superior qualities.

## Evaporation Technique

The first major area of investigation was concerned with the evaluation of dielectric materials. The second major area of investigation is concerned with the treatment and development of the most promising dielectric film. The second area of investigation includes evaporation technique, post evaporation technique, and the determination of fundamental properties of the dielectric film. Evaporation technique includes surface preparation, evaporation at different pressures, evaporation at different rates, condensation on substrates at various temperatures, and the inclusion of other materials in the dielectric film to modify its properties.

Surface preparation is extremely important in the application of any film to a base material. Paints, electrodeposited metals, waxes, and other coatings are applied to properly treated surfaces. In capacitor production, the coatings have to be more nearly perfect than in most other coating work. Since the films are so thin and must be free from pores and uniformly thick, the surface preparation is extremely important. Early experiments were performed to test the effect of surface preparation. Even dirty surfaces were coated with metals or silicon monoxide. Many of the coatings on uncleaned glass surfaces appeared to be sound when seen with the naked eye. Microscopic examination revealed the many imperfections in the coatings applied to uncleaned surfaces. The electrical properties were found to be significantly affected by the quality of surface preparation. Several different cleaning techniques were investigated as described in the section entitled Procedure. The present cleaning technique as described produces microscopically clean surfaces and capacitors having good electrical properties. Better cleaning techniques, however, might improve the electrical properties or stability of the films. Additional cleaning precautions will be investigated in the near future. The electrostatic cleaning of glasses before plating might be an additional help in securing a more perfect base. The elimination of diffusion pump oil vapor may also help in keeping the base clean and in preventing contamination during filming.

The dielectric film was evaporated under different pressures in the ball jar. The lowest pressure at which silicon monoxide was evaporated was about 0.01 micron Hg. Since silicon monoxide is a suboxide, it had a tendency to absorb oxygen from the system during the filming operation. The pressure dropped to a very low value as soon as the silicon monoxide was heated to the evaporation temperature. Evaporated silicon monoxide absorbs oxygen just as the material heated in the crucible absorbs oxygen. When oxygen was added to the system during the filming of silicon monoxide, the dielectric film contained more oxygen than it would normally have contained. If the evaporation was done very slowly in an atmosphere of oxygen, the dielectric film approached the composition of silicon dioxide. If the evaporation was

done rapidly, the dielectric film was composed essentially of silicon monoxide. Therefore, both the rate of evaporation and the partial pressure of oxygen in the vacuum chamber were important. The rate of evaporation was very hard to control and has not been mastered as yet. The pressure in the vacuum chamber was difficult to control at first but is controlled in a routine manner at the present time by regulating the rate of decomposition of copper oxide.

Silicon monoxide has a higher dielectric constant than silicon dioxide but a lower dielectric strength. In addition, films of silicon monoxide are quite stable, whereas thick films of silicon dioxide almost always peel. The best combination of properties are possessed by films lying somewhere between the silicon monoxide and silicon dioxide compositions.

Several methods of controlling the oxygen content of the dielectric were possible. Atmospheric air could be admitted directly into the vacuum chamber. This method of controlling the pressure is practiced in some laboratories but was not investigated on this contract. Instead, pure oxygen was generated in the unit itself. The first method investigated was the method of mixing silicon dioxide and silicon monoxide in a single crucible and heating the mixture. The results of this investigation are listed in Table 2. Some fairly good quality capacitors were produced but the process was quite unwieldy. The second method of adding oxygen during the evaporation process was the decomposition of copper oxide in a separately shielded crucible. The results of this method of adding oxygen are summarized in Table 3. Good quality capacitors were consistently produced with the right combination of metal films, heat treatment, surface preparation, etc. Of the eighty capacitors produced in test number 100, fifty of them had a capacity of about 0.006 m f per square inch of capacitor and over 10,000 megohms resistance at 100 vdc for a 0.004 m f capacitor.

The mechanical stability or peeling problem was encountered throughout the entire period of investigation. Some of the factors responsible for instability of films have already been discussed such as improper cleaning, placing of films of vastly different coefficients of expansion side by side, very high oxygen content of the silicon oxide dielectrics, etc. Yet another factor was also responsible for the poor mechanical stability of some of the films. Many of the unstable films curled or rolled into cylinders indicating the stressed condition present in the film itself. Films may be deposited under stress. Controlling the temperature of the substrate very often helps to produce films of greater mechanical stability. Therefore, several tests were conducted with heated substrates in an effort to improve the mechanical properties of the films.

In test number 83, nine silicon monoxide base capacitors were prepared simultaneously. Five of the capacitors were heated during the filming operation and four were unheated. The four unheated capacitors possessed better electrical characteristics than the heated units. All of the units were placed in an oven heated to 400°F for 15 hours. All of the capacitors unheated during the filming operation peeled. The five units heated during filming were intact. The mechanical stability was greatly improved by filming the dielectric on a heated

## TABLE 2

### SiO-SiO$_2$ BASE CAPACITORS

| Test No. | Capacity m f | D | Q | Resistance at 100 vdc megohms | Composition of Powder Evaporated (%) | | | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | SiO | SiO$_2$ | Silica Soot | |
| 47 | 0.0086 | | 0.17 | 50 | 90 | 10 | - | Heat treated |
| 48 | 0.0050 | | 0.16 | 1000 | 90 | 10 | - | Heat treated |
| 54 | 0.0155 | | 0.036 | 3 | 30 | - | 70 | Heat treated |
| 56 | 0.00575 | | 0.095 | 30 | 48 | - | 52 | Heat treated |
| 58 | 0.0114 | | 0.095 | 5 | 25 | - | 75 | Dielectric thickness--4 wave lengths of visible light |
| 60 | 0.00465 | | 0.050 | 500 | 34 | 33 | 33 | Heat treated |
| 62 | 0.00463 | | 0.095 | 10 | 34 | 33 | 33 | Heat treated |
| 63 | 0.0048 | | 0.032 | 5 | 30 | 40 | 30 | Heat treated |
| 64 | 0.0070 | | 0.024 | 100 | 30 | 40 | 30 | Heat treated |
| 65 | 0.0096 | | 0.0055 | - | 25 | 20 | 55 | |
| 66 | - | | - | - | 25 | 20 | 55 | Thick coating; peeled |
| 68 | 0.0023 | | 0.026 | 50 | 50 / 26 | 50 / 19 | - / 55 | 1st & 3rd coats Second coat Heat treated |
| 69 | 0.0027 | | 0.011 | 1000 | 50 / 26 | 50 / 19 | - / 55 | 1st & 3rd coats Second Coat Heat treated |

## TABLE 3

## SiO BASE CAPACITORS
## FILMED IN 0.2 MICRON O₂ PRESSURE

| Test No. | Average Capacity m f | Average D Q | Average Resistance at 100 vdc megohms | Remarks |
|---|---|---|---|---|
| 95b | 0.0033 | 0.065 | 1,500 | |
| 95c | 0.0035 | 0.04 | 50 | Peeling |
| 95d | 0.0070 | 0.05 | 400 | |
| 95e | 0.00345 | 0.012 | 2,000 | |
| 95f | 0.0026 | 0.007 | 50 to 50,000 | |
| 95g | 0.0035 | 0.041 | 30 | |
| 95h | - | - | - | Slow Evaporation Peeled |
| 95i | - | - | - | Three Dielectric Films; Peeled |
| 95j | - | - | 30 | Heated Base Very Stable |
| 97 | - | - | 30 | Heated Base Very Stable |
| 98 | 0.0050 | 0.011 | 700 | |
| 99a | 0.0030 | 0.010 | 1,500 | Not Very Stable |
| 99b | 0.0040 | 0.025 | 15,000 | |
| 100a | 0.0030 | 0.022 | 14,000 | |
| 100b | 0.0044 | 0.011 | 3,000 | |
| 100c | 0.0050 | 0.016 | 40,000 | |
| 100d | 0.0035 | 0.020 | 15,000 | |
| 100e | 0.0035 | 0.025 | 15,000 | |
| 100f | 0.0042 | 0.019 | 15,000 | |
| 100g | 0.0045 | 0.016 | 10,000 | |
| 100h | - | - | - | Peeled |

## TABLE 3 CONT'D.

### SiO BASE CAPACITORS
### FILMED IN 0.2 MICRON O₂ PRESSURE

Tests 95 and 97      All metal films nichrome

Test 98              All metal films aluminum

Test 99              First film chromium, final film aluminum

Test 100           First film nichrome-chromium, final film aluminum

All capacitors were heat treated at 400°F.

Each number on the table represents an average of 10 units.

substrate although the electrical properties suffered.

In tests number 84 and 85, silicon monoxide base capacitors were filmed with the substrate heated to a higher temperature than in test number 83. All of the units made in both tests were very stable from a mechanical standpoint but the electrical resistance of the dielectric film was less than 10 ohms. Several explanations are possible. The dielectric film might crack or open up fissures during cooling although none were detected. The high temperature of the substrate might accelerate the disproportionation of silicon monoxide in favor of silicon metal and silicon dioxide. Neither of these assumptions has definitely been proven responsible for the low insulation resistance of capacitors heated during the filming operation.

In test number 104, silicon monoxide base capacitors were filmed slowly in 0.2 micron of oxygen on heated substrates. In some cases the dielectric consisted of three films of silicon monoxide heat treated between each filming operation. In this case capacitors of several hundred to several thousand megohms were produced. Additional experimental work must be done on the mechanical stability of dielectric films.

The dielectric film might also be altered by the addition of other materials to the film. The properties of many commercial products are obtained by properly controlled addition of various materials. Rubber products and plastics are significant examples. Some experimental work has already been reported in Table 1 on the addition of fluorides to silicon monoxide dielectrics.

In test number 34, sulfur was filmed along with silicon monoxide to form the dielectric material. The low boiling point of sulfur caused considerable difficulty and evaporation could not be controlled. Sulfur is not a suitable material for vacuum coating. However, a satisfactory capacitor was obtained.

The investigation of various combinations of dielectrics is an inexhaustible field of study. Some additional work in this field may prove fruitful.

## Post Evaporation Technique

At least two post evaporation techniques have proven useful in obtaining better quality capacitors. Capacitors may be heat treated or voltage treated. The voltage treatment consists of applying voltage in excess of the rated voltage of the capacitor. Any weak spots in the unit will burn out leaving a higher resistance unit of approximately the same capacity and lower leakage. Care must be exercised in limiting the applied voltage to some value lower than the general breakdown voltage. If the general breakdown voltage is reached, a considerable portion of the capacitor may burn out wrecking the entire unit.

Heat treating capacitors "sets" the films. The films become harder and more abrasion resistant. The electrical properties are markedly affected. The capacity drops as much as 20% during the heating period. The dissipation factor drops as much as tenfold while the electrical resistance

of the unit increases 100 times or more. The rather loosely knit coating becomes more firm which generally increases the over-all value of the coating tremendously.

Test number 71 was conducted to determine the proper heat treating temperature. A group of six capacitors were heated simultaneously for 30 minutes at a specified temperature. The units were cooled and tested. They were then reheated to a higher temperature than before and again tested. The process was repeated until a heat treating temperature of 800°F had been reached. The 200°F heat treatment produced little change in the units. At 300°F the dissipation factor dropped considerably and the resistance climbed rapidly. The 400°F heat treatment produced additional benefits in dissipation factor and resistance measurements. At 500°F many of the units appeared to lose some of the advantages already gained but the loss was small. As heat treatments continued, the dissipation factor became higher and the electrical resistance decreased. The color of the dielectric film began to change to a lighter color at the 500°F heat treatment and continued to become lighter in color throughout the remainder of the test. Test number 71 indicated an optimum heat treating temperature of 400°F produced capacitors with the best electrical characteristics.

Test number 72 was a repeat test of number 71 over a lower temperature range. Again the 400°F temperature produced superior results.

Test number 75 consisted of a lengthy heat treatment at 300°F followed by a 400°F heat treatment. The electrical properties were tested during the heat treating process and changed slightly during the $4\frac{1}{2}$ hours at 300°F. A subsequent one-hour treatment at 400°F produced considerable improvement again indicating that a 400°F heat treating temperature is superior. Therefore, a standard heat treating temperature of 400°F was used throughout the remainder of the program.

## Properties of Silicon Monoxide

The dielectric constant and dielectric strength are two of the basic properties of dielectric materials. Test number 101 was made to determine the properties of silicon monoxide evaporated slowly in an atmosphere of 0.2 micron of oxygen. The evaporation was carried out by evaporating silicon monoxide rather rapidly for a period of one minute and then more slowly for five additional minutes. This process was repeated until by visual observation the coating appeared to be the correct thickness. The total evaporation time was about 30 minutes. Two sets of 9 capacitors each were produced, the first set being somewhat thinner than the second or normal set. In this way 18 samples of varying thickness of dielectric films were produced. After each evaporation, the capacitors were weighed on an analytical balance to determine the weight of each coating. The capacitors were heat treated at 400°F in the usual way. The results of the 18 capacitor test are listed in Table 4.

The dielectric film was 1 in. by 7/8 in. giving an area of 5.64 cm$^2$. The capacitor area was 3/4 in. by 7/8 in. giving an area of 4.23 cm$^2$. The dimensions of the optical cover glass were 1 1/8 in. by 7/8 in. by 0.008 in. The density of Si is 2.40 g/cm$^3$, [12], SiO is 2.15 g/cm$^3$, and SiO$_2$ is 2.2 g/cm$^3$. The dielectric was assumed to have a density of 2.15 g/cm$^3$.

The capacity of the unit was plotted against the reciprocal of the weight of each unit and compared with the capacity which a fused quartz dielectric of comparable size might have as shown in Figure 1. The dielectric constant was calculated from the dimensional equation

$$\text{Capacitance (m m f)} = 0.08842 \; k \; \frac{\text{Area of film (cm}^2)}{\text{Thickness of film (cm)}}$$

The dielectric constant k for the silicon monoxide base capacitors filmed in 0.2 micron oxygen atmosphere and heat treated at $400^\circ F$ lies between 5.2 and 8.4. An average value of $6.8 \pm 25\%$ represents the dielectric constant of capacitors filmed and treated to produce a good combination of electrical properties.

The thickness of the dielectric film of a high resistance capacitor tested at 100 vdc averages about 0.0006 cm thick. The breakdown voltage usually lies between 300 vdc and 600 vdc. The dielectric strength of the modified silicon monoxide base dielectric lies between 1000 volts/mil and 3000 volts/mil. An average of 2000 volts/mil may be taken as the dielectric strength obtained in these filming operations.
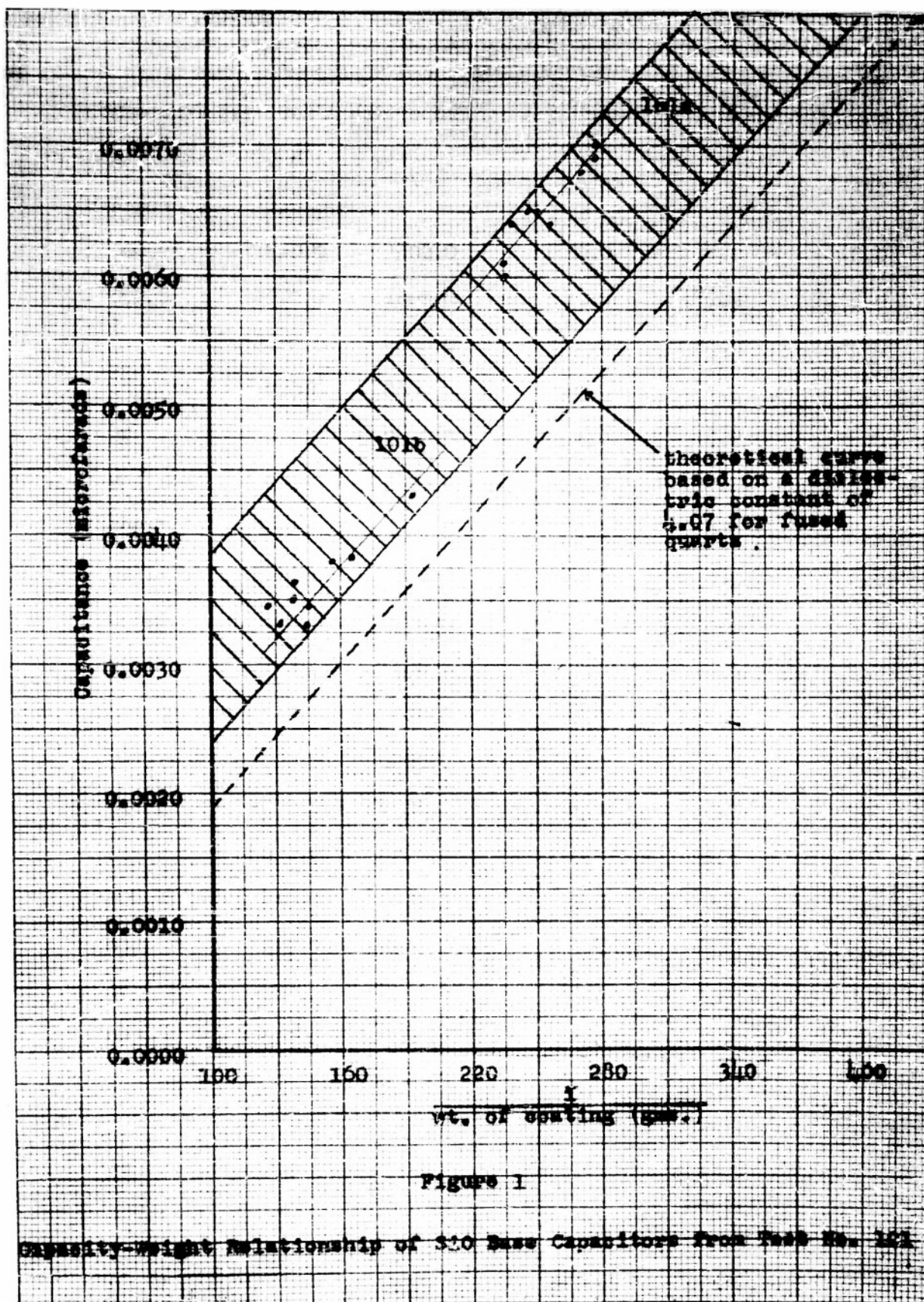
The values of the dielectric constant and dielectric strength of modified silicon monoxide films are compared with the reported properties of fused quartz in the tabulation below:

| Dielectric Constant of Fused Quartz | Dielectric Strength of Fused Quartz volts/mil | Source |
| --- | --- | --- |
| 3.78 | 15,000 | Ref. Data for Radio Engrs. Fed. Tel. & Radio Corp. 67 Broad St., N. Y. |
| 5.0 | 762 | Electric and Magnetic Fields Attwood John Wiley & Sons |
| 3.5 | - | Chemical Engineers' Handbook Perry McGraw-Hill |
| 3.5 - 4.2 | 200 | Radiotron Designer's Handbook Langford-Smith Radio Corp. of America |
| 4.2 | - | Radio Engineers' Handbook Terman McGraw-Hill |
| 4.07 | | Average |
| 6.8 | 2000 | Modified SiO Base Film |

## TABLE 4

### RESULTS OF TEST NUMBER 101

| Wt. of Films (milligrams) | | | Properties after Heat Treatment | | |
|---|---|---|---|---|---|
| 1st metal | Dielectric | 2nd metal | Capacity m f | D Q | Resistance at 100 vdc megohms |
| 0.3 | 4.2 | 0.0 | 0.0064 | 0.017 | 12,000 |
| 0.4 | 4.25 | 0.05 | 0.0061 | 0.0195 | 8,000 |
| 0.35 | 4.05 | 0.0 | 0.0065 | 0.0195 | 6 |
| 0.3 | 3.7 | 0.05 | 0.0068 | 0.020 | - |
| 0.3 | 3.6 | 0.1 | 0.0069 | 0.014 | 75 |
| 0.3 | 3.9 | 0.1 | 0.0064 | 0.019 | 4 |
| 0.3 | 4.05 | 0.0 | 0.0060 | 0.022 | 5,000 |
| 0.3 | 4.0 | 0.05 | 0.0065 | 0.0182 | 3,600 |
| 0.2 | 3.6 | 0.0 | 0.0070 | 0.020 | 3,800 |
| 0.3 | 6.4 | 0.2 | 0.0038 | 0.0175 | 5,000 |
| 0.25 | 7.25 | 0.1 | 0.0036 | 0.0175 | 30,000 |
| 0.3 | 7.8 | 0.3 | 0.0034 | 0.020 | 11,000 |
| 0.2 | 7.5 | 0.3 | 0.0033 | 0.0205 | 9,000 |
| 0.3 | 5.2 | 0.3 | 0.0043 | 0.0103 | 5 |
| 0.3 | 6.0 | 0.2 | 0.0038 | 0.015 | 20,000 |
| 0.3 | 6.9 | 0.2 | 0.0034 | 0.019 | 15,000 |
| 0.4 | 7.3 | 0.2 | 0.0035 | 0.018 | 70 |
| 0.3 | 6.9 | 0.3 | 0.0033 | 0.020 | 14,000 |

Figure 1

Capacity-Weight Relationship of 320 Base Capacitors from Test No. 161

The tabulation of properties allows several important conclusions. Fused quartz is evidently not a completely pure homogeneous material. The variation in both dielectric constant and dielectric strength indicates the variation between different samples of supposedly identical material. The variation of these properties in controlled experimental tests also indicates the importance of physical form and chemical composition. Additional experimental work to improve physical form and chemical composition to achieve the maximum performance from the silicon oxide film is indicated. It is also evident that the inclusion of silicon monoxide in the dielectric film increases the dielectric constant appreciably.

All of the properties of the dielectric films are influenced by the evaporation technique and post evaporation technique as well as composition and purity. The base upon which the capacitor is built might also influence some of the properties, particularly the temperature coefficients. The temperature coefficients have not been determined precisely. The capacitors have not been packaged until very recently and moisture appears to have a pronounced affect upon the properties. In test number 75 the electrical resistance at 100 vdc increased with a rise in temperature up to the boiling point of water after which further heating caused a decrease in electrical resistance. The cooling curve in the same test indicated that the electrical resistance climbed even after passing the boiling point of water. The resistance dropped, however, upon standing unheated overnight. These results emphasize the need for hermetically sealing the capacitor.
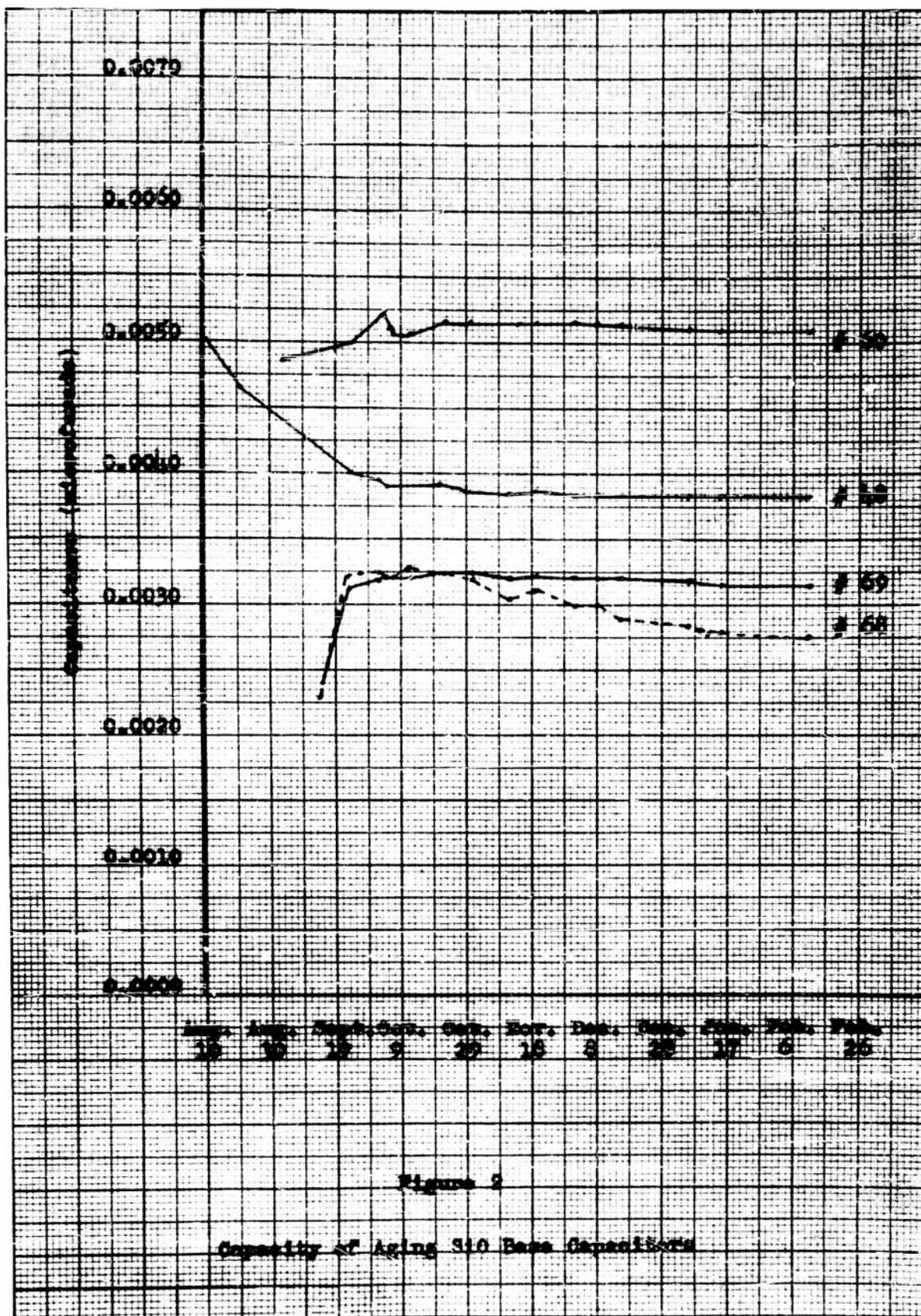
In test number 68 the capacity was measured at various temperatures. The heating and cooling curves did not coincide. The cooling curve was less erratic than the heating curve, and the effect of moisture absorption was indicated again. The capacity of a modified silicon monoxide base capacitor might be expected to change less than 500 p p m per $^{\circ}$C over a temperature range of $100^{\circ}$C to $-40^{\circ}$C.
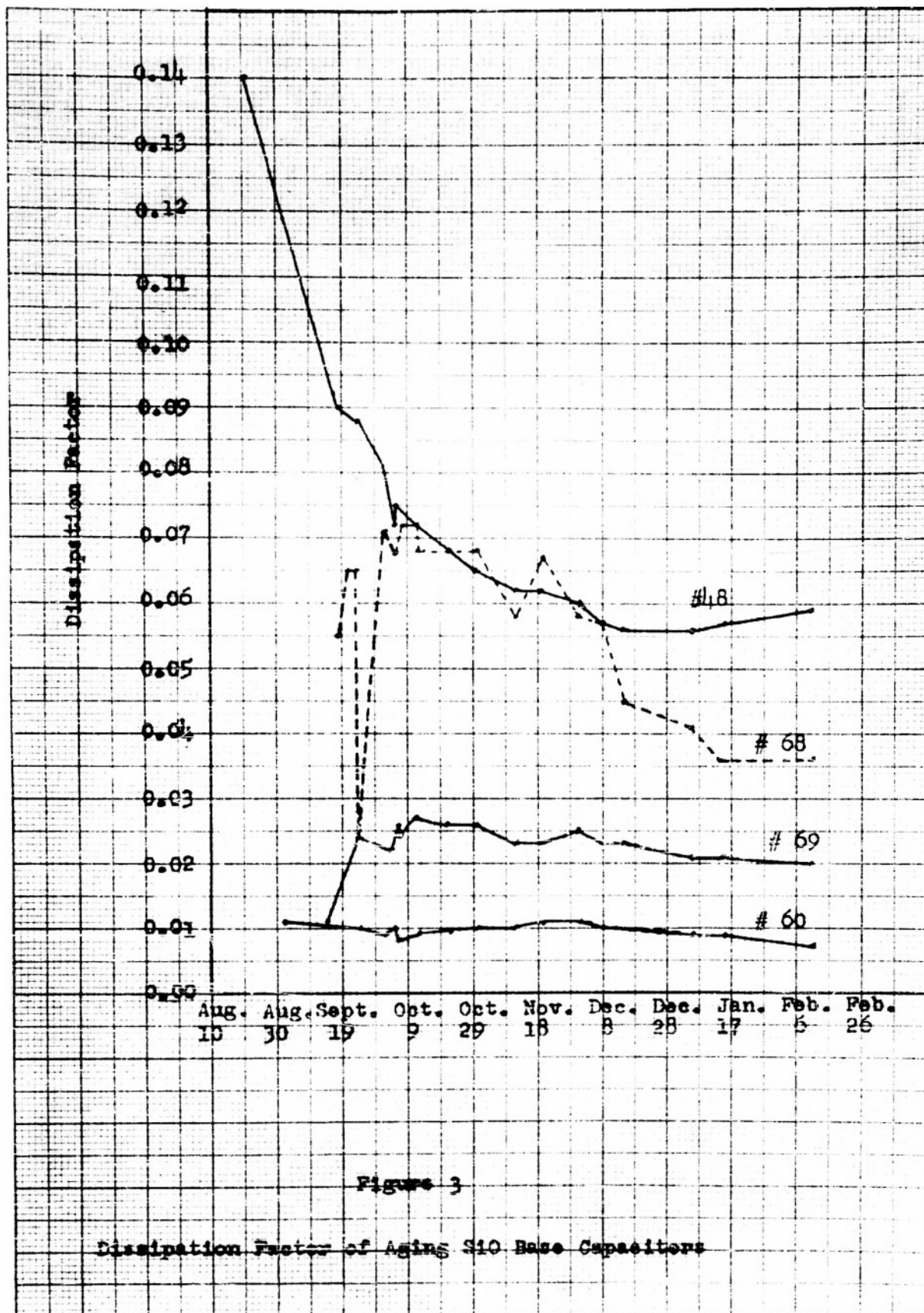
Another important property of the dielectric film is stability. The mechanical stability of good electrical quality capacitors leaves something to be desired. This problem has already been discussed and additional experimental work will be done on this problem. The aging or long time stability is akin to this problem. The shelf life of a product is quite important and some capacitors prepared early in the experimental work were observed over several months duration. The changes in capacity, dissipation factor, and internal resistance are recorded graphically in Figure 2, 3, and 4. The capacity stabilizes; the dissipation factor becomes fairly stable and should improve considerably with proper packaging; the internal resistance increases. The aging characteristics of the modified silicon monoxide dielectric are quite good.
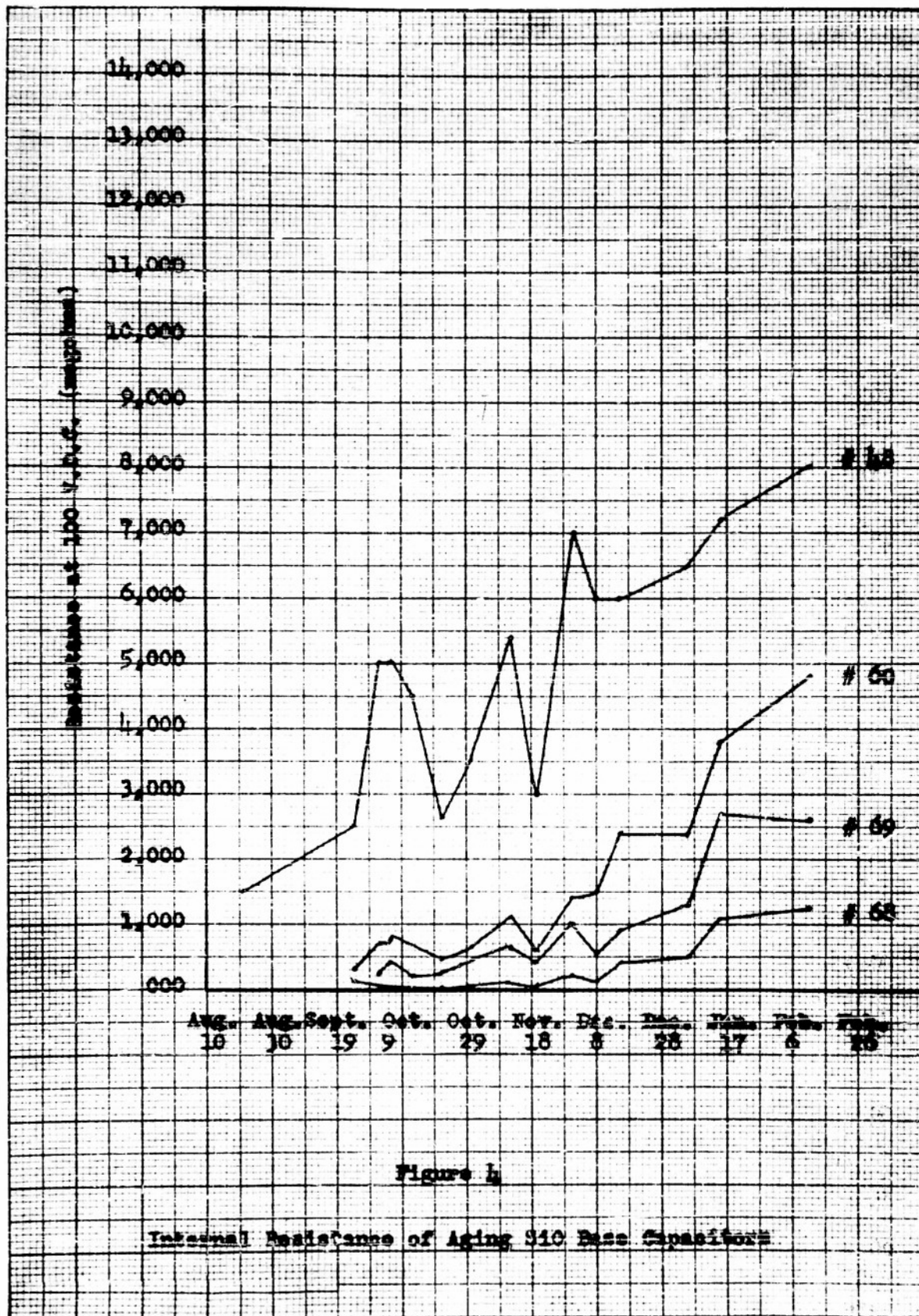
Physical Problems

The physical problems include masking, holding, geometrical limitations, properties of the base, clamps, and packaging material, and the packaging problem itself.

Each capacitor is composed of alternate films of dielectric and metal. These films cannot be simply piled on top of each other but must have a certain geometrical spacing. For instance, each metallic film must be

Figure 2

Capacity of Aging SiO Base Capacitors

Figure 3

Dissipation Factor of Aging SiO Base Capacitors

Figure 4

Internal Resistance of Aging 910 Base Capacitors

accessible so that electrical connections can be made to it. Furthermore the metal films cannot be allowed to touch each other at any spot. All films should be uniform in thickness, smooth, and with sharp boundaries. The capacitor area defined as the area of overlapping of the metal films should occupy as large a portion of the base as is practical.

Materials evaporated in vacuum travel in straight lines from the point of evaporation to the target. Since the source of evaporation is a filament, crucible, or boat, the evaporation does not come from a point source, and shadow effects are rough and ragged. The mask must be close to the target to eliminate scattering of the deposit. If the mask directing metal to a certain area of the base could be changed so that dielectric material would be directed to the proper area, successive evaporations of metal and dielectric could be made without admitting air to the vacuum chamber and subsequently pumping the system down again. A considerable saving in time could be realized. Successive evaporation is possible because the evaporated material travels in straight lines and does not bend around corners. The metal and dielectric could be shielded from each other yet both being visible to the target area. The early experimental tests were conducted with a rotary three-hole mask directing the initial metal, the dielectric material, and the final metal to their respective positions in a single pump down cycle.

The problem of masking must be evaluated constantly at all stages of production. The problems are entirely different for different shaped capacitor bases, and different types of vacuum coating units.

The problem of holding the capacitor base through various stages of processing is also quite important. The capacitor base must be completely clean before filming. The capacitor base is usually held with tweezers during the cleaning operation. Thereafter, the base is handled only by touching its edges.

During the filming operation, the base must be anchored in place to prevent it from moving due to vibration. Various types of clamps have been used as well as tape and positioning bars. Clamps and metal positioning bars are to be preferred over tape, rubber, or other organic or porous substance. The clamping or holding of an optical cover glass (0.008 in. thick) securely but without damage to the glass presents a difficult problem. In this case, the positioning bar method appears to be superior to clamping.

During electrical testing, the capacitor is held in the broad flat contacts of a low compression clip. The description of the method of holding the capacitor in the package will be taken up as a separate topic.

Several geometrical problems and limitations must be satisfied in the design of the capacitor. From a practical point of view, the capacitor must have some simple conventional shape. It should not have arms, joints, or bends. The capacitor should be designed to occupy as small a space as is practical. A cube, short cylinder, or parallelepiped are preferred configurations. The filming of capacitors on flat surfaces lends itself to the preparation of a cubic or parallelepiped capacitor.

All dielectric materials are in powder or lump form. They must be vaporized from a crucible, boat, or other container. The dielectric material must be evaporated upward and condensed on the underside of the base. The entire area of the base cannot be coated because the support for the base masks off part of the area. It is impractical to hold the base by its edges alone. It is also impractical to trim the edges after coating, since the films might be damaged in the process. This geometrical limitation is not serious because the metal films do not extend the full width of the capacitor and the dielectric film does not cover the full length. The base may be supported along both sides during the metal evaporation and along both ends during the dielectric filming. The support area is limited to four very small corners of the base in the case of multiple masks not serving themselves as supports. A compromise solution to the problem may have to be sought in this case.

Other geometrical problems exist in selecting the proper base on which the capacitor is built. The capacitor should occupy as little space as possible. Therefore, the base should be as thin as possible to conserve space and lighten the unit. The base, however, should be thick enough to support the capacitor without crumbling or failing mechanically. The optical cover glass of 0.008 inches thick appears to be about the optimum thickness.

The dielectric film must overlap the capacitor area on all sides to make sure that the metal films have no chance to touch each other. The metal films themselves must be longer than the dielectric film to allow for electrical connection. A greater capacitor area per total area of base will be possible if a rectangular base is used instead of a square base. The electrical connections should be made to the short sides of the rectangular base.

The properties of the materials used are also important. For instance, the capacitor base should not have a large coefficient of thermal expansion. The expansion and contraction of the base governs the size of the entire unit and may add greatly to the thermal stresses set up between the base and the various films. The base should be strong enough to support itself and the films without bending or deforming.

The electrical properties of the base are also important. The electrical resistance must be high and water absorption nil. These properties are important according to the present capacitor configuration. If the geometry is changed, the properties of the base may be changed radically. A metal base with good electrical conductivity can be used if one metal film is completely isolated from the base by dielectric material. The present configuration, however, requires the base to have high electrical resistance.

The optical cover glass is quite thin and might be useful as a dielectric itself. The capacity of thin optical cover glass with metal films on either side of the glass is about 200 m m f per square inch of glass. The cover glass will normally have capacitors filmed on both sides of the glass and the additional capacity of the glass itself may be added to the unit if the electrical characteristics of the glass are satisfactory. In test number 102, nine cover glasses were coated with metal on each side of the glass to form a capacitor. The nine units were packaged together and tested. The electrical resistance was 100,000 megohms at room temperature and the capacity

was 0.0013 m f with a dissipation factor of 0.006. The unit was heated and the electrical resistance measured. The electrical resistance dropped considerably as shown in Figure 5. Test number 102 proved that the capacity of the glass base cannot be accepted because of the poor electrical characteristics of the glass. In addition, it cast considerable doubt upon the quality of the electrical characteristics of capacitors having both metal films anchored to the base itself.

The physical properties of clamps and packaging material must also be investigated. The clamps must maintain sufficient strength, good electrical connections, and must be chemically stable with respect to its surroundings. All packaging material must be stable over the entire temperature range of operation.

The problem of attaching a lead wire to a metal film is not easy. If the metal film is anchored to a glass base, several methods are possible. A low melting indium solder may be used to solder directly to the glass or metal. The softening point of this solder is only 240°F and thus, indium base solder cannot be relied upon to hold high temperature capacitor plates during normal operation. Firing silver applied to the glass before filming and cured at 1100°F furnishes an excellent means of connecting lead wires to the plates themselves. Unfortunately, optical cover glasses warp at these high temperatures and filming becomes extremely difficult.

The mechanical clamping and holding of the glasses may be possible. A solid copper bus was machined to serve as a connector for glass plates. Slots 0.008 inches wide were milled 0.005 inches apart. Glasses were slipped in the slotted busses and tested. These busses did not make sufficiently good contact with the metal films. However, some other method of clamping may be successful.

Individual clips were prepared and slipped over each glass. Several glasses were stacked and soldered together. These clips did not hold very well and were generally unsatisfactory. When tinned clips were used and the pack soldered together, the solder seemed to adhere to the surface of the glasses so that a pack of 10 glasses could not be pulled apart with 10 pounds of force. This type of connection is satisfactory but some improvement may have to be made if the capacitor is operated at high temperature.

A temporary package was designed to house a pack of 15 glasses soldered together. A steel mold (see Figure 6) was made to form halves of a package from cellulose acetate sheet stock. The pack of glass capacitors was slipped into the halves of the plastic package and the halves of the package were sealed together with acetone. The lead wires were sealed with gutta percha. This temporary package will be used to evaluate temperature coefficients at low temperatures and to study aging in the package as compared to aging in atmosphere.

## VI. DISCUSSION

Many dielectric materials have been investigated. The salt type dielectrics appear to be limited to low resistance, rather porous films. Salts are not generally acceptable as dielectric materials although they
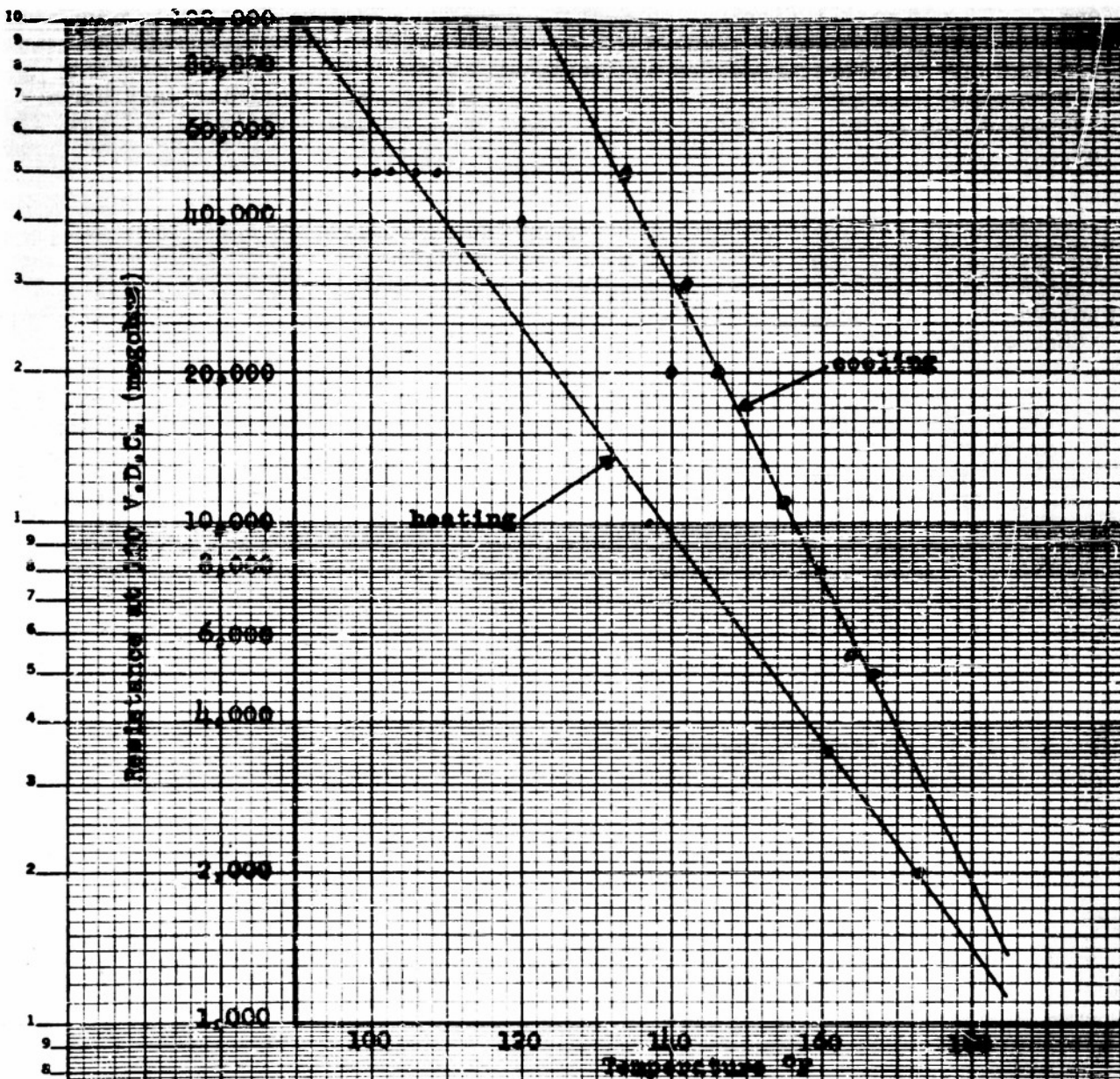
Figure 5

Test No. ___  Electrical Resistance of 2 Optical
cover glasses in parallel with voltage applied
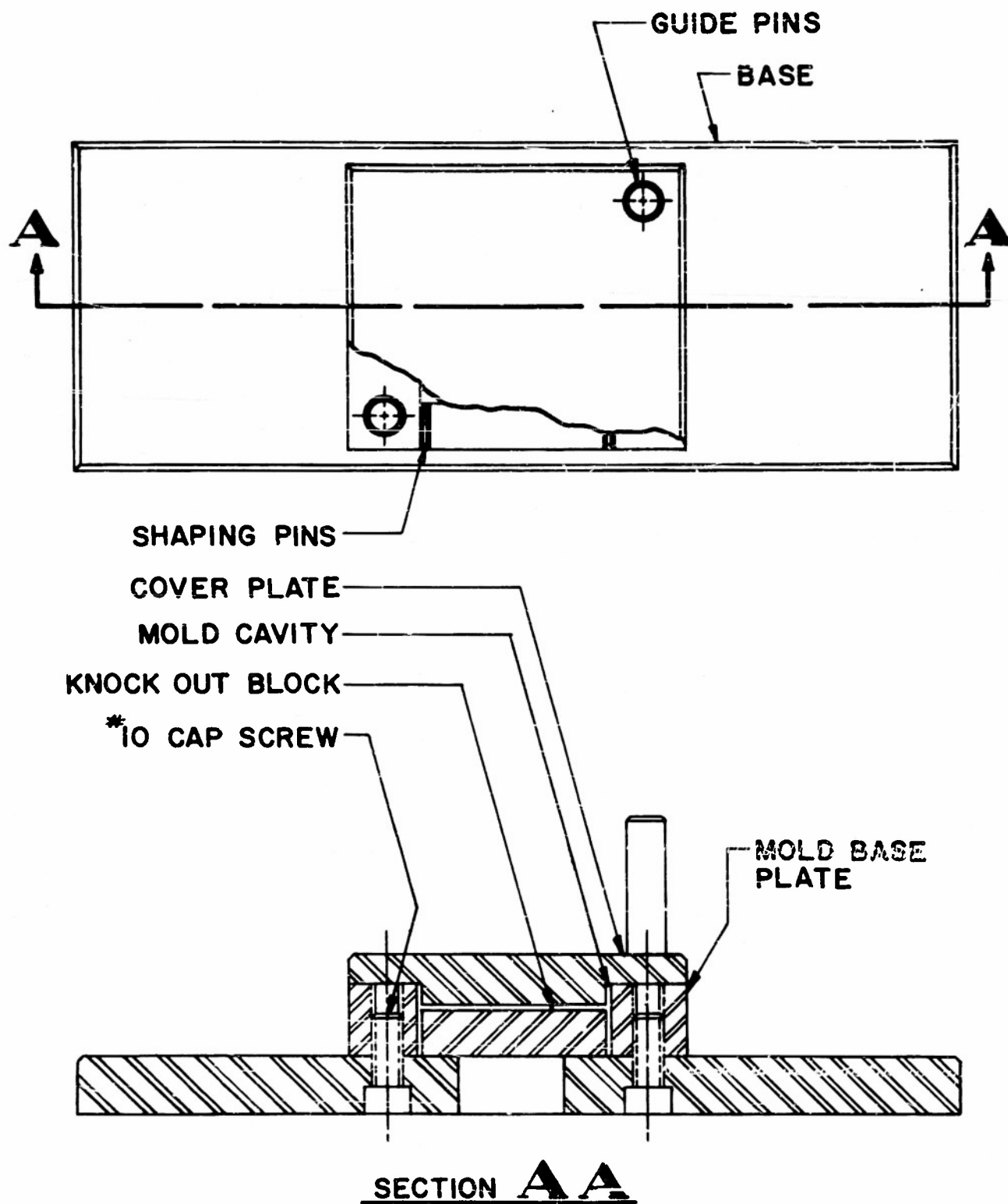to metal film on either side of each glass.

may prove useful in combination dielectrics. The oxides are usually unstable and those oxides which are stable generally do not possess good electrical or mechanical properties. The suboxides of the refractory oxides appear to offer the best combination of properties for filming. Silicon monoxide in particular seems to be the most promising dielectric material.

Many techniques have been investigated in an effort to improve the properties of the silicon monoxide base dielectric film. Satisfactory capacitors have been made with the proper cleaning technique, the right choice of metal films, filming the silicon monoxide slowly in an atmosphere of 0.2 micron of oxygen, a 400°F post evaporation heat treatment, and a voltage treatment.

Not all of the promising dielectric materials have been investigated. Likewise, many techniques and properties of the films have yet to be evaluated. However, during the first part of the experimental program significant advancement in knowledge and in quality of the capacitors produced have been achieved. Some of the major achievements are:

1. Screening of many dielectric materials and determining their relative merit.

2. Detailed evaluation of the silicon oxide dielectrics.

   a. Decomposition of silicon dioxide during evaporation.

   b. The controlled addition of oxygen during a slow filming of silicon monoxide produces a film more quartz-like in nature.

   c. The filming of silicon monoxide on a hot substrate improves the mechanical stability but decreases the electrical resistance of the film.

   d. The determination of an optimum post evaporation heat treatment.

   e. The evaluation of the dielectric constant and dielectric strength of modified silicon monoxide dielectrics.

3. Evaluation of physical problems.

   a. Demonstration test of making an entire capacitor in a single evacuation cycle.

   b. Initial work on packaging resulted in the production of a temporary package for testing.

These advancements in knowledge and technique have added to the prior state of the art. It is now possible to look forward with renewed

GUIDE PINS

BASE

A       A

SHAPING PINS

COVER PLATE

MOLD CAVITY

KNOCK OUT BLOCK

#10 CAP SCREW

MOLD BASE
PLATE

SECTION AA

SCALE: FULL SIZE

FIGURE 6 CAPACITOR PACKAGE MOLD

hope and understanding. The micronic capacitor is advancing from the stage of a seven dielectric film laboratory curiosity of rather low capacity to a single dielectric film production item of greatly increased capacity. Many problems remain unsolved but the future is bright.

## VII. CONCLUSIONS

The modified silicon monoxide film shows excellent promise of becoming an outstanding dielectric material. Additional experimental work should be conducted with this type of film to improve the mechanical stability and electrical properties. Glow discharge cleaning and better quality control should be inaugurated. Additional work should be done on controlling the rate of evaporation.

Better packaging is a requirement which must be satisfied. Various types of tests including life and heat tests must be made.

Planning for the next phases of the work including pilot plant production should start as soon as possible.

Of course, other dielectrics and combinations of dielectrics should not be forgotten and a continual program might be valuable in selecting new dielectric materials or in improving the quality of established dielectrics.

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